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Degradation of nitrobenzene at near neutral pH using Fe^{2+}–glutamate complex as a homogeneous Fenton catalyst

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ABSTRACT

We examined the degradation of nitrobenzene (NB) by modified Fenton reaction at near neutral pH conditions using Fe^{II}–glutamate complex as a source of Fe^{2+}. The reaction was conducted using 0.04 mM (5 mg L^{-1}) of NB in presence of 65 mM H_2O_2 at room temperature. Complex concentrations of 5, 10, 15 and 20 mM (Fe^{2+} = 0.81, 1.62, 2.43 and 3.23 mM) were assayed and showed effective rates of NB degradation with $t_{1/2}$ values of 17, 6.2, 4.8 and 1.85 min, respectively. In the pH range 5–7 the complex activity is pH-dependent, and the optimal pH was 6.3. The degradation was monitored by solid-phase microextraction in combination with GC analysis. The rate of degradation recorded at near neutral pH in presence of 20 mM of Fe-complex was equal to that obtained in presence of Fe^{2+} (2.5 mM) at pH 2.7. Glutamate complexes formed with Cu^{2+} or Co^{2+} did not show the improved degradation observed in case of Fe–glutamate. Furthermore, the introduction of the chelating agent as a free ion into the reaction medium containing Fe^{2+} did not improve the degradation of NB at neutral pH conditions.

1. Introduction

Nitroaromatic compounds are widely used as raw materials in several industrial processes related to pesticides, explosives, colorants and paper pulp production. Many of these substances, such as nitrobenzene and nitrophenols, are usually found in wastewaters of these industries and are considered potentially toxic [1]. Thus, nitrobenzene is listed as a priority pollutant and its maximum allowable concentration is 1 mg L^{-1} in wastewaters [2]; even lower values are demanded. The China permissible level in surface water of NB is 0.017 mg L^{-1} as a standard of the water source for drinking water [3]. Such pollutant is refractory to conventional biological treatments [4,5]. Mineralization of nitrobenzene by microorganisms is prohibited due to the toxic and mutagenic effects on biological systems, which derive from nitrobenzene and its transformation metabolites, such as nitrosobenzene, hydroxylaminobenzene and aniline [6].

Advanced oxidation processes (AOPs), hold great promise to provide alternatives for better protection of public health and the environment. In the last decade, these processes have resulted in effective destruction of refractory pollutants [7]. They are based on the generation of highly reactive and oxidizing hydroxyl radicals, and characterized by a common chemical feature: the capability of exploiting the high reactivity of these radicals in driving oxidation processes that are suitable for achieving the complete abatement and thorough mineralization of even less reactive pollutants. In particular, Fenton processes are useful to achieve considerable reductions in the concentrations of aromatic compounds in wastewaters and they are applicable as a pretreatment stage to reduce the effluent toxicity before biological treatment [8–10]. According to the classical interpretation, the active oxidizing species in degradation of organic matter are the hydroxyl radicals, however, some researchers have discussed the participation of iron species with high oxidation states (particularly ferryl ions, FeO^{2+}) [11]. It was found that the degradation of nitroaromatic compounds by Fenton systems is comparable to the results of photolysis, photo catalysis and radiolysis in metal-free systems [12–14]. This presents further support that ($^{\bullet}OH$) radicals are the most important reactive species in this type of processes.

Fenton oxidations take place usually in the acidic range near pH 3 [15]. The mechanism of such process includes many steps during which iron cycles between +2 and +3 oxidation states and hydroxyl radicals, electrophilic oxidants, reacting with most organic contaminants at near diffusion-controlled rates, are generated [16]. At circumneutral pH, the precipitation of Fe^{3+} as hydrous oxyhydroxides, $Fe_2O_3{\cdot}nH_2O$, which does not redissolve readily, inhibits the recycling of Fe^{3+}/Fe^{2+}. Soluble Fe^{2+} salts tend to co-precipitate with Fe^{3+} oxyhydroxides if both ions are present at neutral pH [16]. Modified Fenton processes have gained considerable attention, where chelating agents have been widely used in order to keep the iron in soluble form preventing its precipitation and thus enhance the production of hydroxyl radical and the degradation efficiency [17,18].

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Thus, the use of iron chelates in the Fenton remediation has been extensively studied [15,19–21] because they can be applied at neutral pH. However, the ligands also pose secondary environmental risks because they can mobilize toxic metals [21].

A process of pollution treatment becomes advantageous when it saves time on working with minute pollutant concentrations. On the other hand, the use of safe and environmentally friendly substances in pollution treatment, and avoiding the necessary drastic conditions such as strongly acidic medium, could be of prime importance when the issue of pollution is considered. Park and Choi [22] have reported that amino acids can form metal chelates with ring structure by reacting the alpha amino group and metal ions having a valance of 2 or more e.g. iron, cobalt, manganese, chromium, at pH range 4.5–6.5. The free amino group or carboxyl group of the alpha amino acid neutralizes the cationic charge of the metal ion. Yehia et al. [23] reported recently that the use of glutamic acid has considerably enhanced the dark Fenton degradation of BTEX contaminants at near neutral pH.

The objective of the present study was to evaluate the influence of Fe–glutamate complex that has not been previously reported, on the efficiency of modified Fenton oxidation process for destruction of low content of nitrobenzene in aqueous solution, with the aim of extending the pH range towards neutral conditions. The usual Fenton reaction under acidic conditions was also conducted for comparison. In addition, the possible use of the complexes of copper and cobalt, as homogenous catalysts instead of iron in such process was examined.

2. Materials and methods

2.1. Chemicals

Nitrobenzene (99%) was obtained from Sigma–Aldrich, succinic acid (98%), glutamic acid (99%) and hydrogen peroxide (H_2O_2) (30%, w/v) were purchased from Fluka (USA). $FeSO_4{\cdot}7H_2O$ (99%) from Loba. $CaCO_3$, $CoSO_4{\cdot}7H_2O$ (97%), $Na_2S_2O_3{\cdot}5H_2O$, NaOH (96%), $CuSO_4{\cdot}5H_2O$ (97%), and H_2SO_4 (96%, w/w) were purchased from ADWIC (Cairo, Egypt). All chemicals were used without further purification.

2.2. Preparation of reagents

Aqueous solution of nitrobenzene was prepared on a daily bases (10 mg L^{-1}, that corresponds to 0.081 mM nitrobenzene) using deionized water. The neck of the volumetric flask was sealed with Teflon tape to prevent volatilization. The aqueous solution was magnetically stirred to ensure complete dissolution of the nitrobenzene.

The required mass of iron salt was dissolved in appropriate volume of degassed deionized water while stirring the solution and immediately the pH was adjusted to 2.0–3.0 using dilute H_2SO_4 (0.5–1.0 M). All iron catalyst solutions were prepared immediately prior to the initiation of Fenton oxidation reactions in order to avoid potential flocculation and precipitation of iron salts or iron colloids via reaction with dissolved oxygen (if any). Glutamic acid and succinic acid solutions were prepared by dissolving the appropriate amount of the acid in deionized water that was adjusted to pH 11 by adding 0.1 M NaOH. Hydrogen peroxide concentration (30%, w/v) was justified iodometrically by titration with 0.1 M $Na_2S_2O_3$.

2.3. Preparation of Cu, Co and Fe–glutamic acid chelate

The complexes were prepared according to the recipe of Park and Choi [22]. Calcium carbonate (2 g) was dispersed in 50 mL of water and dissolved therein by stirring, and glutamic acid (6 g) was added to perform a reaction with continued stirring until the calcium carbonate and glutamic acid were entirely dissolved. Next 3 g of metal sulfate was added to the reaction mixture and a white precipitate of calcium sulfate was formed. After incubating the reaction for 30 min, the resulting solution was centrifuged to remove insoluble materials, and the clear supernatant solution was separated. The supernatant was freeze-dried to obtain about 6 g of soluble copper, cobalt or iron–glutamic acid chelate. These chelates have ring structure as presented in Fig. 1. The structure of the complex was acknowledged through agreement of mass balance as described by the original authors, in addition to the IR data. The latter are summarized in Table 1.

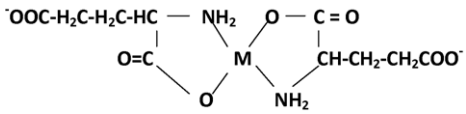


Fig. 1. Structure of metal–glutamate complex.

2.4. Catalytic Fenton and modified Fenton reactions

All reactions were carried out using two-neck flasks (250 mL). The first neck was used for introducing reactant solutions. The second neck was capped with a screw cap having a Teflon-lined septum with a pre-cut opening, through which a pH electrode was introduced. A volume (80 mL) of nitrobenzene solution (10 mg L^{-1}) was mixed with the same volume of aqueous solution containing the required amount of Fe(II) or the metal chelate in case of modified Fenton reaction. To adjust the pH of the solution 0.1 M NaOH was added in order to maintain a nearly constant pH (deviations $\leq$ 0.3 pH units). The reaction was started by adding the appropriate amount of H_2O_2 (1.06 mL of 30%, w/v; density = 1.11 g mL^{-1}). All experiments were conducted in duplicate (two flasks) at room temperature ($25 \pm 2\,^{\circ}C$), in the absence of light. The standard deviation of two replicates was less than 4%. The flasks while wrapped in black plastic foil were shaken at 130 circular rpm. Samples were taken from the same reaction flask after 1, 5, 10, 15, 20, 25, and 30 min. The reaction was quenched instantaneously by adding 2 g of $Na_2S_2O_3$ to withdrawn samples (20 mL) before analysis. Control experiments were conducted by not adding any iron or peroxide. The experimental conditions of different runs are collected in Table 2.

2.5. Data collection and chemical analyses

The concentration of the undegraded nitrobenzene was determined by solid-phase micro extraction (SPME) using 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers (Sigma–Aldrich, Germany) in combination with GC analysis as described in Refs. [24–26]. Briefly, the fiber was introduced through the septum of a vial containing the solution withdrawn from the reaction flask and immersed in the solution for 30 min. During

Table 1
Assignment of IR data of glutamate complex [27].

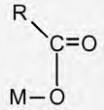
Group	Wavenumber (cm^{-1})
$\upsilon(NH_2)$	3308, 3266
$\upsilon(CH_2, CH)$	2925, 2861
	υ_{as}: 1639; υ_s: 1317
δ(CCN)	544
υ(M–N)	480–497

Table 2
Experimental conditions of Fenton runs carried out at room temperature.

Run	Glutamate (mM)	Complex (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	NB (mM)	pH
Fenton	–	–	2.5	65	0.04	2.7, 5, 6,7
	–	–	2.5, 5, 10	65	0.04	2.7
Modified Fenton	–	5, 10, 15, 20	0.81, 1.62, 2.43, 3.23[a]	65	0.04	6.3
	20	–	2.5	65	0.04	6.3

[a] Concentration of Fe^{2+} in provided complex (M. wt = 346).

this time, the solution was stirred on a magnetic stirrer using glass-coated stirring bar. Afterwards, the fiber was removed and introduced into the GC injector (220 °C 30 min, splitless injection) for desorption of analytes and GC analysis. The degradation of nitrobenzene was monitored by determining the residual concentration remaining after certain periods of reaction using HP 5890 gas chromatograph, provided with a flame ionization detector and equipped with a column (3.048 m in length and 3 mm int. diam.) packed with Benton 34 (5%); diisodecyl phthalate 5% (wt%) on chromsorb W (AW) 80-100 mesh. The initial oven temperature (80 °C) held for 3 min, programmed at 2 °C min−1 to 120 °C (5 min). The injector and the detector temperatures were 250 and 275 °C, respectively. Under these conditions, the retention time for nitrobenzene was 20.2 min.

3. Results and discussion

3.1. The Fenton reaction

3.1.1. Effect of pH

The results of nitrobenzene (NB) degradation, 0.04 mM, by Fenton reagent at different pH values in presence of 65 mM H_2O_2 and 2.5 mM Fe^{2+} are shown in Fig. 2. It has to be noted that the headspace over reaction mixture upon extracting the last sample for analysis (30 min) is effectively different from that over the initial points. However, the noted complete degradation of NB within 10 min, and the small differences between the last reading and the preceding ones, in case of incomplete degradation, implies that this effect did not reduce strongly the accuracy of the points taken at latter stages of degradation. Furthermore, the results of control data support this conclusion. It can be seen that both the degradation rate and efficiency have decreased with the increase in the working pH. Rapid degradation occurs initially because of an abundance of •OH generated from H_2O_2 decomposition via reaction (1) [28]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (k = 63\ M^{-1}s^{-1}) \qquad (1)$$

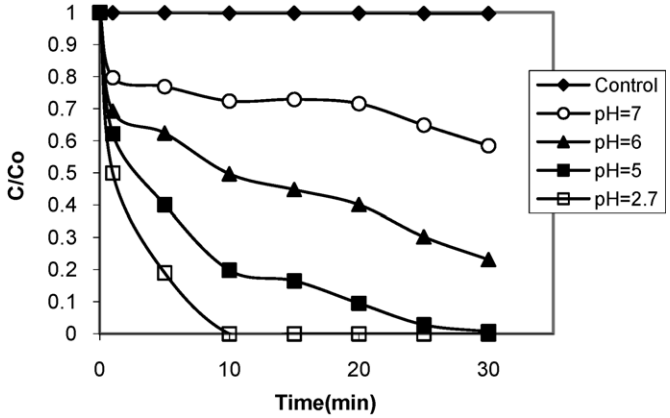


Fig. 2. Effect of pH on NB degradation: H_2O_2 = 65 mM; NB = 0.04 mM; Fe^{2+} = 2.5 mM.

The formed •OH radicals from reaction (1) could rapidly degrade nitrobenzene through a reaction of rate constant $3.9 \times 10^9\ M^{-1}\ s^{-1}$ [28]. Furthermore, the rate of the reaction between Fe^{2+} and H_2O_2 increases with increasing pH [29], and the formed Fe^{3+} in reaction (1) continues the cycle of Fenton reaction through further decomposition of H_2O_2 and regenerating Fe^{2+} (reaction (2)) [28]:

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\bullet} + Fe^{2+} + H^+ \quad (k = 10^{-3}\text{–}10^{-2}\ M^{-1}\ s^{-1}) \qquad (2)$$

However, the lower rate constant of reaction (2) than reaction (1) makes the former the rate-determining step. The decrease in the rate of nitrobenzene decomposition at pH values higher than 2.7 can be in part attributed to the controlling role of formed Fe^{3+}. Furthermore, at a pH above 4 the dissolved fraction of iron species decreases as a colloidal ferric species that form insoluble precipitates of amorphous Fe^{3+}-oxyhydroxides, which produce very low yields of oxidants from reaction with H_2O_2 [30,31]. In addition, at these pH values (5–7), the reaction of Fe^{2+} with H_2O_2 does not always produce •OH. The oxidant formed at neutral pH values, which is believed to be the ferryl ion [Fe(IV)], is capable of oxidizing short chain aliphatic alcohols and arsenite, but cannot oxidize aromatic compounds and other recalcitrant contaminants [21]. Therefore, the decreased rate and decomposition efficiency recorded at pH values 5–7 can be understood based on both slowing down the recycling of Fenton's reagent and decreasing the amount of available Fe ions necessary for producing •OH radicals through the reaction with H_2O_2. The decrease of the oxidation rate at the initial stage as the pH increases has been reported previously [32,33]. Also, results of other researchers showed that NB can be completely degraded even at higher contents, for example 5 and 7.5 mM of nitrobenzene could be oxidized completely in 10 and 30 min, respectively [33].

3.1.2. Effect of Fe^{2+} concentration

To inspect the effect of Fe^{2+} concentration on NB (0.04 mM) degradation we conducted the experiments in presence of 2.5, 5.0 and 10 mM of Fe^{2+} with 65 mM H_2O_2, at room temperature and pH 2.7. The results showed that increasing the Fe^{2+} concentration has a negative effect on the rate of NB degradation i.e. the rate decreases as the Fe^{2+} concentration increases, Fig. 3. It is generally accepted that with increasing ferrous salt concentration, degradation rate of organic compounds also increases, but only to certain level where further addition of iron becomes inefficient [34,35]. The results of nitrobenzene degradation via Fenton reaction, furthermore, appear to show dependence on reaction conditions. For $[PhNO_2]_o$ = 0.1 mM in presence of $[H_2O_2]_o$ = 3.9 mM, $[FeCl_2]_o$ = 0.035 mM, the half-life time of degradation was 360 min [36,a]. Increasing the concentration of H_2O_2 to 8.0 mM, keeping the concentrations of Fe and $PhNO_2$ the same as in the previous study has resulted in decreasing $t_{1/2}$ to 250 min [36,b]. This indicates that, in general, the increase in reaction rate may take place on decreasing the Fe/H_2O_2 ratio, when Fe concentration is held constant. In our case, where H_2O_2 concentration is held constant, the values of $t_{1/2}$ varied as 2.0 min (k = 0.346 min^{-1}), 4.0 min (k = 0.1698 min^{-1}) and 5.9 min (k = 0.117 min^{-1}) for Fe^{2+} concentrations of 2.5, 5.0 and 10 mM, respectively. This also indicates the increase in reaction rate

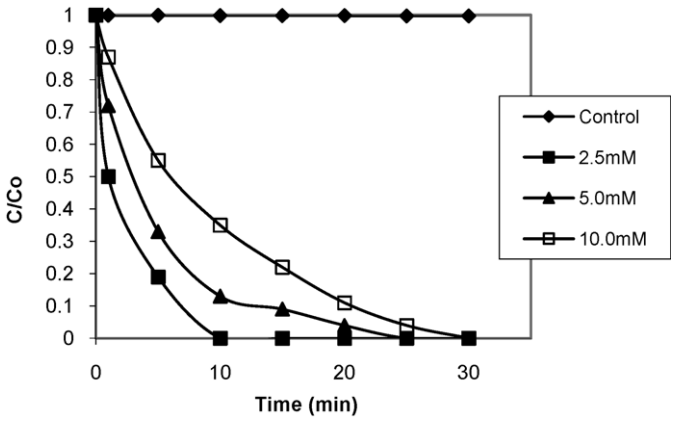


Fig. 3. Effect of Fe concentration on NB degradation at pH 2.7, H_2O_2 = 65 mM, NB = 0.04 mM.

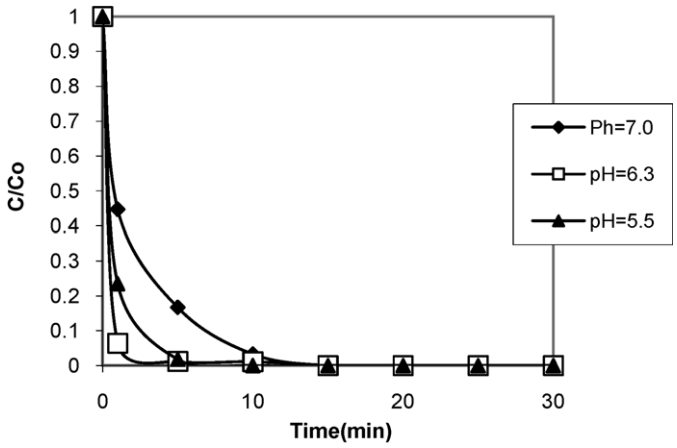


Fig. 4. Effect of pH on NB degradation by Fe–glutamate: H_2O_2 = 65 mM; NB = 0.04 mM; Fe–glutamate = 20 mM.

on decreasing the Fe/H_2O_2 ratio when H_2O_2 concentration is kept constant.

The reaction between Fe^{2+} and H_2O_2 produces a sufficiently •OH within a short period ($k = 63\ M^{-1}\ s^{-1}$). The lifetime of the hydroxyl radical is determined by its reactions with nitrobenzene ($k = 3.9 \times 10^9\ M^{-1}\ s^{-1}$) and other present •OH scavengers: Fe^{2+} ($k = 4.3 \times 10^8\ M^{-1}\ s^{-1}$) and H_2O_2 ($k = 2.7 \times 10^7\ M^{-1}\ s^{-1}$) [28]. The fraction of •OH that reacts with nitrobenzene ($f^{\bullet}_{OH,NB}$) can be expressed by Eq. (3), similar to that proposed by Lee and Sedlak [21]:

$$f^{\bullet}_{OH,NB} = \frac{k^{\bullet}_{OH,NB}[NB]}{k^{\bullet}_{OH,NB}[NB] + k^{\bullet}_{OH,H_2O_2}[H_2O_2] + k^{\bullet}_{OH,Fe}[Fe^{2+}]} \quad (3)$$

Considering that [NB] is constant, then the major variables are [H_2O_2] and [Fe^{2+}] which may control the change in $f^{\bullet}_{OH,NB}$. However, despite [H_2O_2] will change with change in Fe^{2+} concentration, yet its lower rate constant of reaction with •OH than that of Fe^{2+} makes the change in [Fe^{2+}] more effective in changing $f^{\bullet}_{OH,NB}$ specially in case of higher Fe content. Therefore, since the available Fe^{2+} ions to act as •OH scavenger will increase with the increase in $[Fe^{2+}]_o$ we can expect, according to Eq. (3), the decrease in $f^{\bullet}_{OH,NB}$ with the increase in $[Fe^{2+}]_o$, and consequently a decrease in NB degradation rate which explains the trend shown in Fig. 3. Yoon et al. [37] have reported that when the Fenton reaction was initiated by a high concentration of Fe^{2+} (usually more than 1 mM) a sufficiently •OH was produced with a short time. They indicated that under these conditions, the scavenging of •OH by Fe^{2+} becomes important at high $[Fe^{2+}]_o/[H_2O_2]$ ratio. Furthermore, at higher Fe^{2+} concentration, the formed Fe^{3+} could be expected to increase so that, due to very low reaction rate constant with H_2O_2 (reaction (2)), the recycling of Fenton reaction is greatly slowed down resulting in a slower rate of NB decomposition upon increasing Fe^{2+} concentration. Generally, the latter effect appears of lower significance than the scavenging effect, unless precipitation is clearly detected.

3.2. Modified Fenton reaction

3.2.1. Choice of optimal pH

To select the best pH conditions at which we can test the used Fe–glutamate in NB degradation via modified Fenton reaction, we have worked at three arbitrarily selected pH values, mainly 7, 6.3 and 5.5. The results obtained and shown in Fig. 4 indicate that pH 6.3 is the optimal among the three examined values. The reason for this pH-dependent behavior of Fe–glutamate is not clear at present since according to Park and Choi [22] the stability of the complex is pH-independent in this range. However, according to the results at hand, we checked the activity of different concentrations of the complex in NB degradation at the optimal pH i.e. pH 6.3.

3.2.2. Effect of complex concentration

The degradation of NB in presence of Fe–glutamate complex was followed at pH 6.3 using 5, 10, 15 and 20 mM of the complex as Fe^{2+} source (0.81, 1.62, 2.43 and 3.23 mM), with $[NB]_o$ = 0.04 mM, $[H_2O_2]_o$ = 65 mM, at room temperature, Fig. 5. The degradation rate in presence of the complex at all concentrations was faster than in its absence (Fe^{2+} = 2.5 mM) and among the different concentrations decreased in the order 20 > 15 > 10 > 5 mM. The degradation rate in case of 20 mM complex was enormously fast showing 95% decomposition after 1 min, and an overall activity with $t_{1/2}$ = 1.85 min ($k = 0.3748\ min^{-1}$). The concentration of 5 mM complex was not enough to decompose NB completely during 30 min, whereas 10 and 15 mM have resulted in total decomposition after 30 min, with the latter of higher rate. The $t_{1/2}$ values were 17 ($k = 0.0407\ min^{-1}$), 6.24 ($k = 0.1111\ min^{-1}$) and 4.81 min ($k = 0.1441\ min^{-1}$) for 5, 10 and 15 mM, respectively. On the other hand, working with Fe^{2+} without chelation has resulted in only 30% decomposition after 30 min ($t_{1/2}$ = 94.9 min). The rate of NB degradation in presence of 20 mM Fe–glutamate at pH 6.3 is equal to that obtained in presence of 2.5 mM Fe^{2+} at pH 2.7. In their study of the effect of humic substances as a chelating agent on Fenton treatment of wastewater, Lipczynska-Kochany and Kochany [16] have found that at pH 7 the removal of all studied substances (toluene, o-, p-, and m-xylene, and dichloromethane) in the presence of HS (3000 mg L^{-1}) was comparable to that at pH 3.5 without HS. The presence of Fe^{2+}

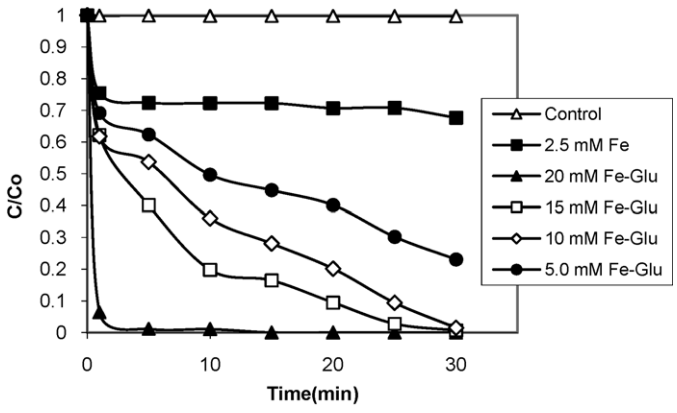


Fig. 5. Effect of Fe–glutamate complex on NB degradation at pH 6.3, H_2O_2 = 65 mM, NB = 0.04 mM.

as a chelated species appears successful in extending the working pH for pollutants abatement via Fenton reaction to the neutral or near neutral region.

The mechanism of the considered catalytic reaction is out the scope of the present study, furthermore, to describe a mechanistic degradation we have to have at least some idea about the possible intermediates which are subject of debate. In Fenton homogeneous system at near neutral pH, the chelating agent could maintain iron in soluble form preventing its precipitation and thus enhance the production of hydroxyl radical and the degradation efficiency [17,19]. Furthermore, chelated-Fe^{2+} react with H_2O_2 more rapidly than Fe^{2+} aqua complexes that increases the rate of •OH formation [20,38,39]. For example, Fe^{2+}–EDTA reacts with H_2O_2 via rate constant of $2 \times 10^4\ M^{-1}\ s^{-1}$ which is faster than that of Fe^{2+} with H_2O_2 ($63\ M^{-1}\ s^{-1}$) [28]. Information about the rate constant of the reaction of Fe^{2+}–glutamate with H_2O_2 is lacking [28]; however, we can use the following reaction pathways to interpret the very fast degradation of NB in presence of Fe^{2+}–glutamate complex:

$$Fe^{2+}\text{–glutamate} + H_2O_2 \rightarrow Fe^{3+}\text{–glutamate} + {}^{\bullet}OH + HO^- \quad (4)$$

$$^{\bullet}OH + H_2O_2 \rightarrow O_2{}^{\bullet-} + H^+ + H_2O \quad (5)$$

$$O_2{}^{\bullet-} + Fe^{3+}\text{–glutamate} \rightarrow Fe^{2+}\text{–glutamate} + O_2 \quad (6)$$

The hydroxyl radicals produced in reaction (4) participate in NB degradation ($k = 3.9 \times 10^9\ M^{-1}\ s^{-1}$), and in producing $O_2{}^{\bullet-}$ through reaction (5) ($k = 2.7 \times 10^7 M^{-1}\ s^{-1}$) [40,41] that regenerates Fe^{2+}–glutamate through reaction (6). Therefore, the recycling of the process takes place that results in formation of new •OH radicals through reaction (4). Since the generation of Fe^{2+} from Fe^{3+} is the rate-limiting step in Fenton reaction, the presence of glutamate chelating agent can therefore considerably improve the overall modified Fenton oxidation reaction of NB. It would be expected the reaction of $O_2{}^{\bullet-}$ with Fe^{3+}–glutamate to be faster than that with Fe^{3+} as it is reported in case of Fe^{3+}–EDTA and Fe^{3+} [20]. The observed increase in rate with increasing the complex concentration can be attributed to the increased amount of •OH produced through reaction (4). Furthermore, the formation of Fe^{3+} as a complexed species prevents its precipitation that occurs in absence of the chelating agent. It should be noted that although the rate constant of the second order reaction of NB with •OH is higher than that of H_2O_2, yet under the conditions of 65 mM H_2O_2 and 0.04 mM NB, •OH radicals will be scavenged by H_2O_2 and NB with a pseudo-first order rate constants of 1.75×10^6 and $1.56 \times 10^5\ s^{-1}$, respectively. This explains the participation of H_2O_2 in reaction (5) that causes the recycling of the process.

The fact that complexed Fe^{2+} also reacts faster than free Fe^{2+} with •OH [28] makes it possible the scavenging of the latter by available Fe^{2+}–glutamate that may decelerate the rate of NB decomposition. In addition, Fe^{2+}–glutamate actually consumes equivalent amount of •OH in its regeneration via reaction (6) by $O_2{}^{\bullet-}$ produced in reaction (5). However, it seems that the fast rate of NB reaction with •OH and the involvement of Fe^{2+}–glutamate, initially present plus newly formed through reaction (6), in reaction with H_2O_2 (reaction (4)), producing more •OH, have overcome the scavenging effect of Fe-complex. One would expect that if the scavenging activity of the complex was taking place effectively, a decrease rather than an increase in NB degradation will be the result of increasing the complex concentration, which is not the case. Therefore, it is clear that the negative effect noted at pH 2.7 of increasing Fe^{2+} concentration is not taking place in the case of using complexed Fe^{2+} at near neutral pH.

To interpret the change in NB degradation rate with complex concentration we have to consider other •OH scavenging reactions [28]:

$$^{\bullet}OH + O_2{}^{\bullet-} \rightarrow OH^- + O_2 \quad (k = 0.7\text{–}1.0 \times 10^{10}\ M^{-1}\ s^{-1}) \quad (7)$$

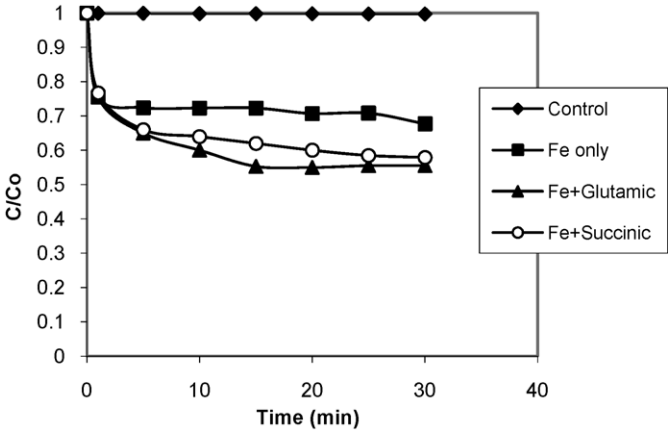


Fig. 6. Effect of chelating agent (20 mM) on NB degradation at pH 6.3, H_2O_2 = 65 mM, NB = 0.04 mM, Fe = 2.5 mM.

$$2\,^{\bullet}OH \rightarrow H_2O_2 \quad (k = 5.2\text{–}6.2 \times 10^9\ M^{-1}\ s^{-1}) \quad (8)$$

A concentration of 5 mM, presumably resulted in a limited amount of •OH of which a considerable fraction is consumed in reactions like (7) and (8), and therefore the remained part necessary for complete NB degradation during 30 min was insufficient. Increasing the complex concentration to 10 and 15 mM resulted in increasing the production of •OH so that complete NB degradation was effected after 30 min. However, the gradual profile of degradation in the case of these two concentrations implies that different radical scavengers were competing during the period of 30 min.

At a concentration of 20 mM the production of •OH was apparently high enough to furnish sufficient amount necessary to degrade the present content of NB within few minutes.

At neutral conditions, formation of Fe(IV), ferryl ion, as the predominant oxidant takes place [42,43]. This oxidant is more selective than hydroxyl radical in its reaction with organic compounds [44]. The role of this oxidant seems marginal in our case.

While no detailed mechanism can be extracted from the presented results, yet it can be inferred that the formed intermediates due to NB degradation at near neutral pH, under the applied conditions, are not intervening in the Fenton reaction due to clear absence of any lag periods in the decomposition profiles.

3.2.3. *Effect of complex formation*

We followed the degradation of NB at pH 6.3 in presence of Fe^{2+} (2.5 mM) and glutamic acid (20 mM) when they were added separately. The obtained results under these conditions, Fig. 6, indicated that the presence of the glutamate complexing agent did not improve the degradation behavior of NB in contrast to the case in which it was first complexed with Fe^{2+}, Fig. 5. The slow rate and incomplete degradation of NB within 30 min can be interpreted as inability of free glutamate ions to complex Fe^{2+} ions that entered in reaction with H_2O_2 as conventional Fenton reaction. The complication of Fe^{3+} formation at neutral conditions in addition to the expected formation of Fe(IV) may be responsible for the observed results. The reaction of Fe(IV) with •OH has a rate constant of $1.0 \times 10^7\ M^{-1}\ s^{-1}$, while with NB is $1.05 \times 10^3\ M^{-1}\ s^{-1}$ [11], therefore the scavenging ability of Fe(IV) for •OH is much higher than its oxidation activity towards NB. The free glutamate would also act as •OH scavenger due to the high reaction rate constant ($k = 2.3 \times 10^8\ M^{-1}\ s^{-1}$) [28]. This was confirmed by using 20 mM succinate ($pk_{a1} = 4.2$; $pk_{a2} = 5.6$) instead of glutamate, for which the reaction rate constant with •OH ($k = 3.1 \times 10^8\ M^{-1}\ s^{-1}$) is practically equal to that of glutamate [28]. The results presented in Fig. 6 imply the correctness of the proposed •OH scavenging by glutamate if introduced into the reaction medium as free ions at

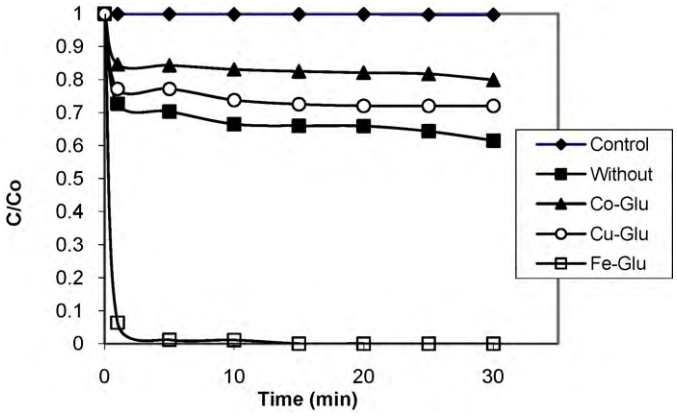


Fig. 7. Effect of complexes on NB degradation at pH 6.3, H_2O_2 = 65 mM, NB = 0.04 mM, complex = 20 mM, Fe = 2.5 mM.

near neutral conditions. It appears that as the complexation process has improved the activity of Fe^{2+}, it also improved the stability of glutamate towards hydroxyl radicals.

3.2.4. Modified Fenton using Cu– or Co–glutamates

To test the probability of using other transition metals chelated by glutamate in the degradation process of NB at near neutral conditions, we followed the degradation in presence of 20 mM Cu–glutamate or Co–glutamate, Fig. 7. The results have indicated that both complexes are not good catalysts for the reaction under study. In spite of the fact that Fenton-like reaction can be accomplished by other transition elements than iron [45], yet it seems that we have to take into account the stability of the used complex [20]. The greater the value of the formation constant, the higher is the affinity of the metal ion for the ligands and consequently the higher complex stability. The formation constants, log K_f, for Fe–, Co–, and Cu–glutamate complexes are 4.6, 5.06 and 7.85, respectively [46]. Therefore, the higher activity of Fe–glutamate than that of the Cu and Co complexes could be attributed, in part, to the differences in complex stability. This point may need further study.

4. Conclusions

The introduction of Fe^{2+} as Fe–glutamate complex into Fenton reaction can extend and improve the rate of nitrobenzene degradation process into neutral pH conditions. The optimal pH value is 6.3. The complex preserves the needed Fe^{2+} as a soluble species even at near neutral pH, and probably prevents the expected precipitation of formed Fe^{3+} known as a delaying stage within the recycling of iron species taking place in Fenton reaction. It seems, however, that the complex formation is a pre-requisite for such improvement to occur as we have found that the addition of the complexing agent and Fe^{2+} separately did not result in any improvement at neutral conditions. This was interpreted as scavenging of $^{\bullet}OH$ by glutamate ions, and/or due to the formation of Fe(IV) species of low reaction rate with NB, but of higher scavenging rate to $^{\bullet}OH$. The very fast rate of NB degradation at near neutral pH recorded in case of 20 mM Fe–glutamate complex does make sense regarding the minute amount of pollutant studied (0.04 mM). This makes the applied treatment method a promising way of pollutant abatement in short time. The glutamate complexes with copper or cobalt do not appear successful as that of iron in the reaction under study under the used conditions. The variable stability of formed complexes may be the reason; however, more experiments are needed to support this suggestion. Using higher NB concentrations with Fe–glutamate or testing other amino acids than glutamic merit the consideration in future works.

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